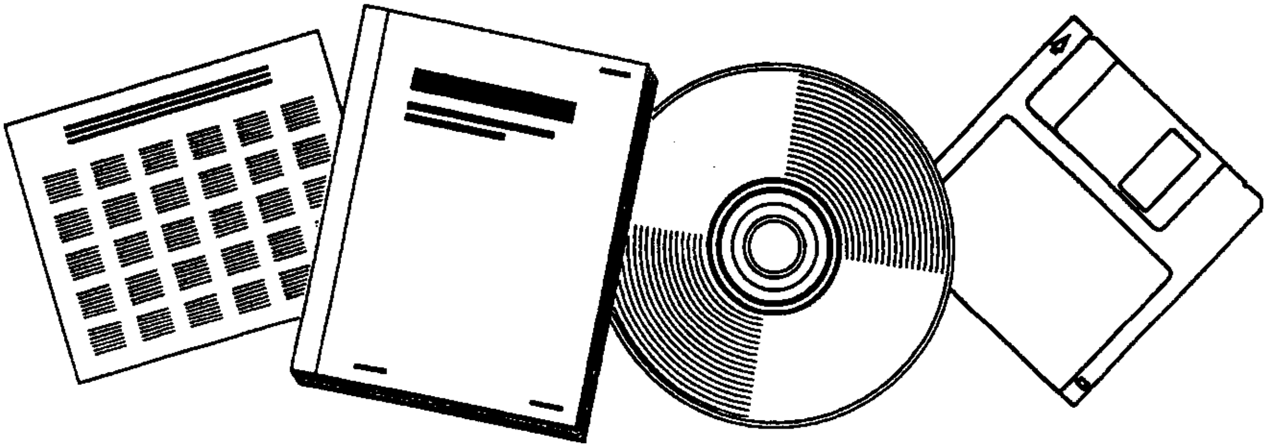
SLURRY-PHASE FISCHER-TROPSCH SYNTHESIS

DEPARTMENT OF ENERGY, PITTSBURGH, PA.
PITTSBURGH ENERGY TECHNOLOGY CENTER

1986



Presented at Indirect Liquefaction
Contractors' Conf., Monroeville, PA
December 2-4, 1986 - will be published in Proceedin

SLURRY-PHASE FISCHER-TROPSCH SYNTHESIS

CONF-861288--1

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CONF-861288--1

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Fischer-Tropsch (F-T) synthesis in the slurry phase has attracted attention in recent years due to its numerous advantages (See Figure 1 and discussions in References 1-3). Among these advantages are the ability of the liquid phase to handle the large heats of reaction and thereby control reaction temperature, the ability to handle low H_2/CO ratio synthesis gas without needing a preliminary water-gas shift step,[4] and the relatively low capital and operating costs for slurry systems.[3] Slurry-phase work at PETC has focused on understanding effects of catalyst preparation and pretreatment, of reaction conditions (T, P, H_2/CO), and of operating conditions (space velocity, methods of wax removal) on catalyst synthesis behavior (activity, selectivity, and maintenance of activity and selectivity). Better understanding of the effects of these factors on F-T synthesis leads to improvements in process technology.

This work focuses on the effects of catalyst pretreatment on synthesis behavior. Developing an effective F-T catalyst pretreatment procedure is a problem limited almost exclusively to iron catalysts (Figure 2). A ruthenium, cobalt, or nickel catalyst is almost always reduced at 475-725 K in flowing H_2 before F-T synthesis. The goal of this pretreatment is to reduce the Ru, Co, or Ni to the zero-valent state for subsequent synthesis.

Even over a wide variety of conditions, these catalysts remain reduced during F-T synthesis.

The purpose of pretreatment for iron F-T catalysts is not nearly so clear. Reduction in H_2 to zero-valent iron is one possible pretreatment, but does not give results analogous to those obtained with other F-T catalysts. While the H_2-reduced catalysts may initially be zero-valent iron, in syngas it is rapidly converted to a carbide phase or phases;[5,6] at higher syngas conversions, the accumulation of the products H_2O and CO_2 makes the gas mixture oxidizing, so Fe_3O_4 is also formed.[7] Thus, the catalyst composition changes during synthesis. Other pretreatments often yield a better catalyst than obtained by H_2-reduction. In none of these pretreatments is the catalyst converted to zero-valent iron, but the catalyst composition still changes during synthesis. Therefore, the only clear goals of pretreatment are the general goals of obtaining high activity, the desired selectivity, and long life. It is then not surprising that effective pretreatment for iron catalysts have been developed empirically, and that no one pretreatment is universally used for each catalyst preparation.

This paper reports some recent results on the effects of pretreatment. Synthesis runs were made using one of two different pretreatments given a potassium-promoted precipitated iron catalyst (Figure 2). Besides these reaction experiments, catalyst samples were periodically withdrawn from the stirred autoclave for characterization by means of Mössbauer spectroscopy.

EXPERIMENTAL PROCEDURES

The method of catalyst preparation is summarized in Figure 3. A catalyst precursor was prepared in a continuous precipitation unit described elsewhere.[8] In this unit, a flowing aqueous solution of $Fe(NO_3)_3$ and $Cu(NO_3)_2$ was mixed with another flowing solution of NH_4OH. The pH of precipitation was measured with a pH meter and was controlled at pH = 7.0 by adjusting the flow rate of the NH_4OH solutions. The precipitate obtained was then filtered, washed, and dried in an oven at 383 K for 48 h in N_2, then 24 h in vacuum. Each preparation yielded about 50 g of catalyst precursor. Each batch was analyzed for % Fe, Cu, and O, and for BET surface area and pore volume. Batches of similar composition and surface area were combined and thoroughly mixed into one master batch containing 65% Fe, 0.6% Cu, and the balance oxygen.

Samples of this master batch were impregnated with a K_2CO_3 solution. For each 50 g sample of the master batch to be impregnated, 20 ml of solution were added drop-wise and mixed until the precursor was thoroughly wetted. Each impregnated sample was then oven-dried at 383 K for 24 h. Different concentrations of K_2CO_3 solution were used in order to yield precursor batches containing between 0.11% and 0.29% K. Catalyst without potassium was obtained by using a sample from the original master batch. All experiments described here used precursor samples containing 0.29% K. Before use, each impregnated batch was also calcined in an air oven with temperature raised in a step-wise manner, with a final temperature of 623 K.

Figure 4 is a simplified schematic of the reactor system, described in more detail elsewhere.[8] Figure 5 summarizes the conditions of the two reaction experiments described here. The "induced" catalyst was exposed to a flow of 1/1 H_2/CO syngas at WHSV = 1.75 at 533 K throughout the entire history of the run (WHSV = weight of gas per hour per unit weight of catalyst). The "CO-pretreated" catalyst was also exposed to a flow of CO at WHSV = 1.63 at 553 K for 24 h before exposure to synthesis conditions. (The space velocities of CO flow in the CO-pretreatment and during synthesis were identical). In each experiment, 25 g of calcined catalyst precursor was charged to a stirred autoclave containing 320 g of purified n-octacosane wax. Reactor pressure was 200 psig and impeller speed on the autoclave was held at 1000 rpm throughout each run. Catalyst samples were taken during reaction runs for Mössbauer spectroscopy and X-ray diffraction analysis; procedures of sample withdrawal were similar to those described previously.[9]

RESULTS

Catalyst activity and selectivity with time on stream are shown in Figures 6-8 and in Table 1 for each run. For the induced catalyst, percent H_2 and percent CO conversions were initially substantial but declined threefold during 400 hours on stream. In contrast, the initial activity for the CO-pretreated catalyst was strikingly high, with both percent CO and percent H_2 conversions approaching the maximum achievable (Figure 6). Furthermore, this activity declined slowly with time on stream.

Figure 7 and Table 1 show the overall selectivity of the induced catalyst. This catalyst initially favored production of C_{5+} liquids and wax, with less than 14% of hydrocarbon in the C_1-C_4 range after 96 hours. Nevertheless, catalyst selectivity shifted to lighter products during synthesis. The percentage of wax in the product dropped from 61.0 at 96 hours to only 30.5 after 359 hours on stream, while percent C_1-C_4 increased to 22.7. Thus, catalyst deactivation was accompanied by a shift in selectivity towards lighter products.

Figure 8 and Table 1 show the same information for the CO-pretreated catalyst. This catalyst initially made a very light product. After 96 hours in syngas, 26.0% of the hydrocarbon was in the C_1-C_4 range, while 31.1% of the hydrocarbon was wax. This initially light selectivity can be attributed to the initially very high percent CO conversions, which produced a very high H_2/CO ratio in the reactor. For this run, the usage ratio of H_2/CO was 0.6/1-0.7/1, much lower than the inlet feed ratio of 1/1. Thus, H_2CO ratios in the reactor always exceeded 1/1, and were initially higher than 6/1. The decrease in CO conversion over time correlated with increased selectivity to heavier products. After 200 h on stream or longer, the H_2/CO ratio in the reactor was in the same range as present initially with the induced catalyst, and catalyst selectivities during these time periods were very similar. For the remainder of the run with the CO-pretreated catalyst, selectivity continued to shift towards heavier products, as CO conversion, and thus, H_2/CO ratio, continued to drop.

Selectivity differences attributable to secondary reactions of primary F-T products were not major. For the induced catalyst, the olefins in the C_2-C_4 fraction was essentially constant at 80% over the life of the run (Figure 9). For the CO-pretreated catalyst, the percent olefins in C_2-C_4

fraction was initially below 70% but continuously increased as CO conversion decreased. After 400 hours on stream, the percent olefins in the C_2-C_4 fraction approached 85%. This increase in percent olefins as percent conversion decreased is consistent with the idea that olefins are primary F-T products.[10]

Figure 10 shows the degree of approach to equilibrium in the water-gas shift reaction. For each catalyst, the ratio $[(H_2)(CO_2)]/[(H_2O)(CO)]$ is below the equilibrium value of 73 and declines with time on stream. The sharpest degree of decline was observed with the induced catalyst, which also showed the sharpest activity loss. This is consistent with the idea that H_2O, not CO_2, is the primary oxygenated product, and that CO_2 arises mainly from secondary water-gas shift reaction of product H_2O with CO.[11] Again, the extent of a secondary reaction, the water-gas shift reaction, decreased as overall conversion to primary products decreased.

Figure 11 shows room temperature Mössbauer spectra of catalyst samples withdrawn either after CO-pretreatment or after pretreatment and exposure to syngas. (The spectra are raw data, with no superimposed computer fits). Figure 11 also indicates the expected peak positions for the two sextets in Fe_3O_4,[12] the single sextet for ε' carbide,[5] and the three sextets of the χ-carbide phase.[13] The spectrum (not shown) of the calcined catalyst precursor was indistinguishable from bulk α-Fe_2O_3. The first spectrum in Figure 11 shows that during 24 h pretreatment in CO, the catalyst was essentially completely reduced/carbided to χ-carbide, although traces of Fe_3O_4 peaks are still visible in this spectrum. Following 24 hours in syngas, the carbide spectrum is diminished while an Fe_3O_4 component is clearly visible. After

72 hours on stream, more oxidation to Fe_3O_4 had occurred at the expense of the carbide. No further changes are visible in the spectrum of the sample taken after 310 hours in syngas. These spectra show that the χ-carbide phase was oxidized at the high syngas conversions obtained with this catalyst. This oxidation at high syngas conversions occurs mainly because of the high partial pressure of H_2O at these conditions.[7]

Figure 12 shows Mössbauer spectra for the induced catalyst after 24 h and after 503 h in syngas. After 24 h the catalyst was carbided mainly to the hexagonal ε'-carbide, with small amounts of χ-carbide also present. After 503 h the Fe_3O_4 component had disappeared, and the catalyst was completely carbided.

CONCLUSIONS

Conclusions are summarized in Figure 13. With the CO-pretreated catalyst, activity was initially very high and declined slowly over time. During the early periods of the run, selectivity favored light hydrocarbons but shifted over time to heavier, more olefinic products. Mössbauer spectra showed that the pretreated catalyst was essentially 100% carbide, mainly χ-carbide, but was substantially oxidized to Fe_3O_4 during the first 72 hours of synthesis.

Both the initial selectivity to light hydrocarbons and oxidation of the CO-pretreated catalyst can be attributed to the initially high syngas conversions. High syngas conversions produced an H_2/CO ratio greater than 6/1 in the reactor, favoring a lighter, more paraffinic product than would be favored at lower H_2/CO ratios. The high syngas conversions produced H_2O concentrations high enough to oxidize the catalyst. Nevertheless, oxidation produced no dramatic effects on catalyst activity.

The induced catalyst had slightly lower initial activity than the CO-pretreated catalyst, but also deactivated much more rapidly. After about 200 hours on stream a shift in selectivity towards C_1-C_4 gases and away from wax production became noticeable. The catalyst composition, which was mainly ε'-carbide and Fe_3O_4 after 24 hours on stream, was completely converted to carbide phases during the run. No oxidation was observed during this run, which reflects the lower syngas conversions and thus, the lower percent H_2O in this run.

The higher activity of the CO-pretreated catalyst can result from at least two types of effects:

1. Physical: Higher specific surface area (m^2/g).
2. Chemical: Higher intrinsic activity per m^2 of surface.

Physical measurements currently under way (BET surface area, average crystallite size from X-ray diffraction line broadening) will help determine to what degree differences in surface area influence the observed differences in activity for the two catalysts. Since not only initial activity but also long-term activity and selectivity differed on the two catalysts, the intrinsic activity and selectivity of the two catalyst surfaces also was likely to differ. Characterization of catalyst surface properties by means of various electron and ion spectroscopies (Auger, XPS, SIMS, ISS) should help identify differences in the surfaces of each catalyst.

Future reaction experiments will study the effects of these catalyst pretreatments using lower ratio syngas (H_2/CO - 0.7/1). Other variations in pretreatment will also be tested to give a broader picture of factors affecting pretreatment. These experiments, when combined with information obtained from catalyst characterization, will help identify pretreatment factors required to obtain a catalyst with high activity, desired selectivity, and long life.

ACKNOWLEDGEMENT

The authors thank Richard D. Chi for preparing the catalyst, and Ed Bauer, Fred Harke, Jim Nagle, and Harry Woodson for carrying out the reaction experiments. They also wish to thank Dr. V. U. S. Rao and Dr. R. R. Schehl for useful discussions of this work.

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TABLE 1.
ACTIVITY AND SELECTIVITY WITH PRECIPITATED IRON CATALYSTS
(0.29% K; 1/1 H_2/CO, 533 K, 200 psig)

	Induced		**CO-Pretreated**	
Time in syngas (hours)	96	359	95	359
% H_2 Conversion	42.6	13.3	55.5	47.6
% CO Conversion				
Total	73.5	23.3	88.8	80.4
To Hydrocarbons	36.0	10.6	44.3	37.8
Hydrocarbon Distribution				
% CH_4	3.4	6.0	5.1	2.7
C_2-C_4	10.2	16.7	20.9	9.9
C_{5+} liquids	25.4	46.8	42.9	27.0
Wax	61.0	30.5	31.1	60.4

NO./12,997

FIGURE 1.
FISCHER-TROPSCH SYNTHESIS IN THE SLURRY PHASE

- Advantages of Slurry F-T Synthesis:
  - Uniform Reaction T, Good Control of Heat of Reaction ($\Delta H \sim -50$ kcal/mole CO)
  - Low CH_4 Production & C Deposition on Catalyst
  - Can Handle Low H_2/CO Ratio Syngas
  - No Major Heat or Mass Transfer Limitations
  - Simple System → Low Capital, Operating Costs

- Objective of Slurry-Phase Synthesis Studies:

  Understand Effects of
  - Catalyst Pretreatment Methods
  - Reaction Conditions (T, P, H_2/CO)
  - Operating Conditions (% Conversion, Product Removal Methods)

  On
  - Activity
  - Selectivity
  - Activity & Selectivity Maintenance

B&R/10.889

FIGURE 2.

PRETREATMENT EFFECTS ON Fe CATALYSTS

- Purpose of pretreatment clear for most F-T catalysts
  - Ru, Co, Ni reduced in H_2
  - Catalysts stay reduced during synthesis

- Purpose of Fe catalyst pretreatment unclear
  - Active catalyst can contain α-Fe, Fe oxide, Fe carbide(s)
  - Reduction in H_2 one of many pretreatments
  - Pretreated catalyst changes composition during synthesis

- Fe pretreatment very empirical

- **This work** — Effects of two pretreatments
  - (a) "Induction" at synthesis conditions
  - (b) CO-pretreatment

    Mössbauer spectroscopy, X-ray diffraction

FIGURE 3.
SLURRY PHASE F-T SYNTHESIS WITH PRECIPITATED IRON CATALYSTS

- Catalyst prepared in continuous precipitation unit
  - Solution of $Fe(NO_3)_3$ and $Cu(NO_3)_2$ continuously flows into stirred unit
  - Continuous flow of NH_4OH solution gives precipitate
  - Samples filtered and washed, oven-dried

- Impregnation with K_2CO_3 solution
  - Impregnated to wetness
  - Samples oven-dried
  - Calcination in air, final temperature 623 K

- Composition — %Fe 65
  Cu 0.6
  K 0.0-0.29

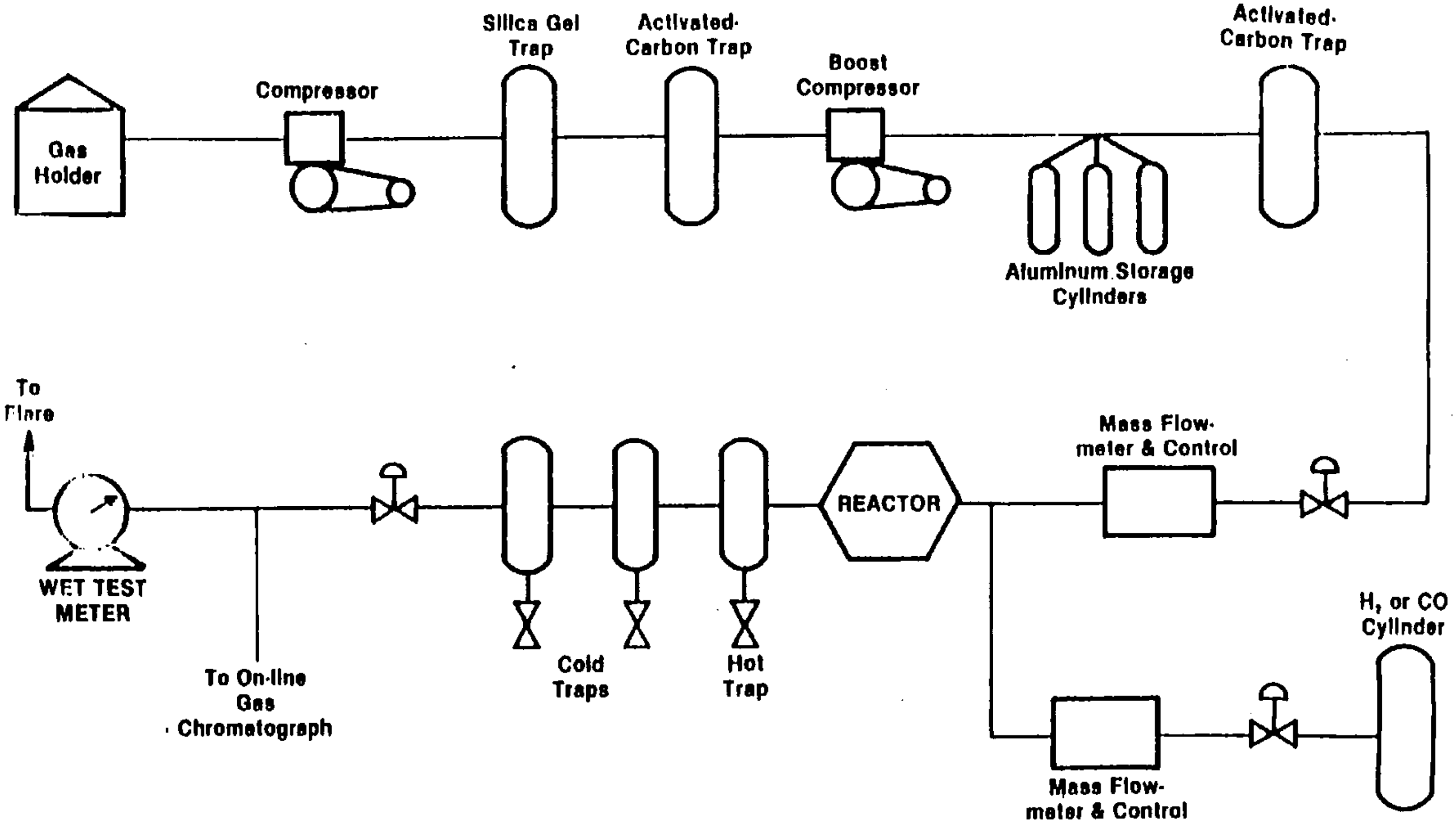

FIGURE 4. SCHEMATIC OF REACTOR SYSTEM.

No. 976

FIGURE 5.
REACTION EXPERIMENTS IN STIRRED AUTOCLAVE

- Calcined Fe/Cu/K suspended in n-octacosane
- Pretreatment: 1/1 H_2/CO 533 K WHSV = 1.75
  CO 553 K WHSV = 1.63
- Reaction Conditions: 1/1 H_2/CO 533 K WHSV = 1.70
- Conditions for
  Pretreatment and Reaction: 200 psig
  25 g catalyst
  320 g n-octacosane
  1000 rpm
- Slurry samples removed for Mössbauer analysis

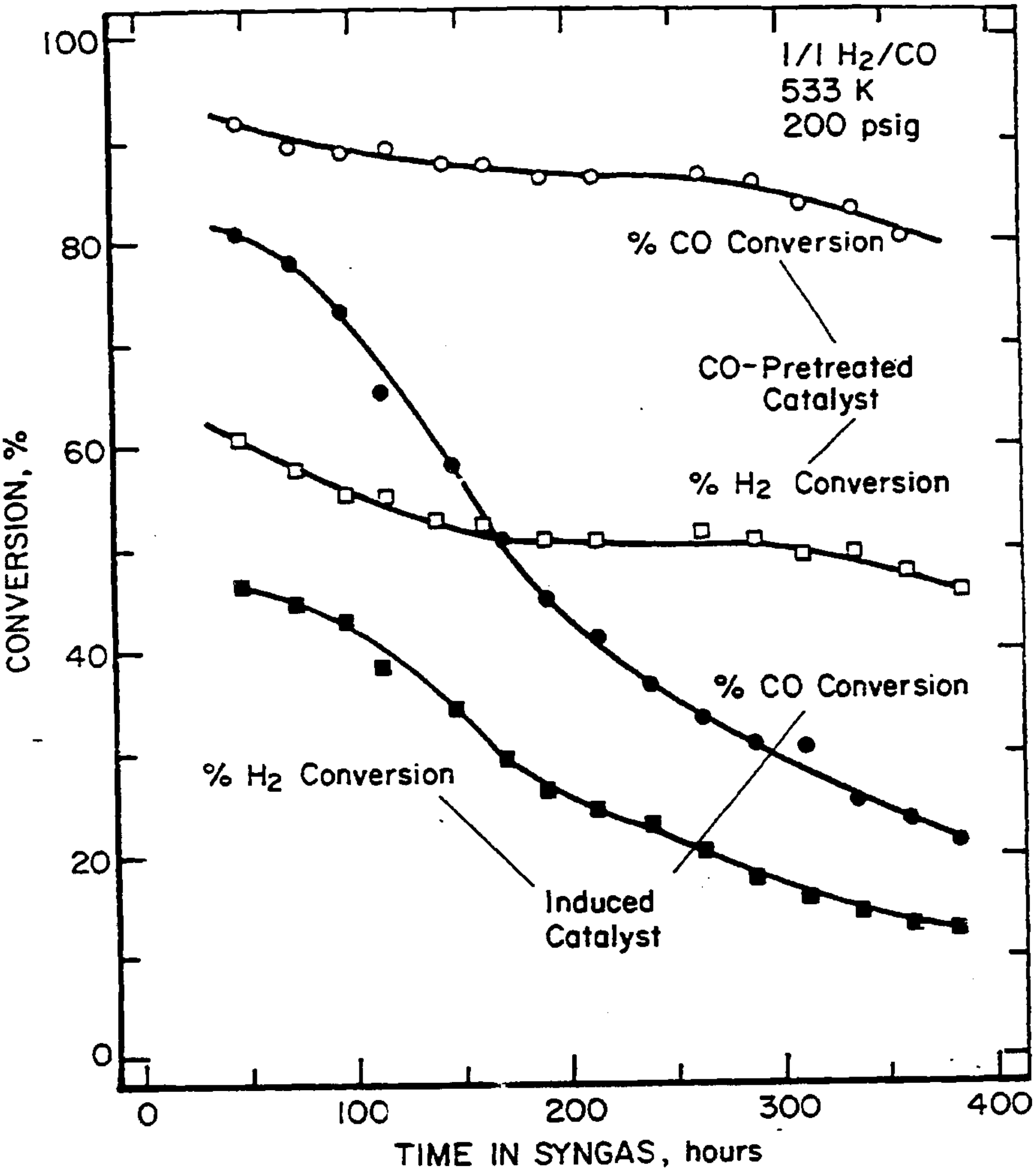

FIGURE 6. CATALYST ACTIVITY VS. TIME ON STREAM

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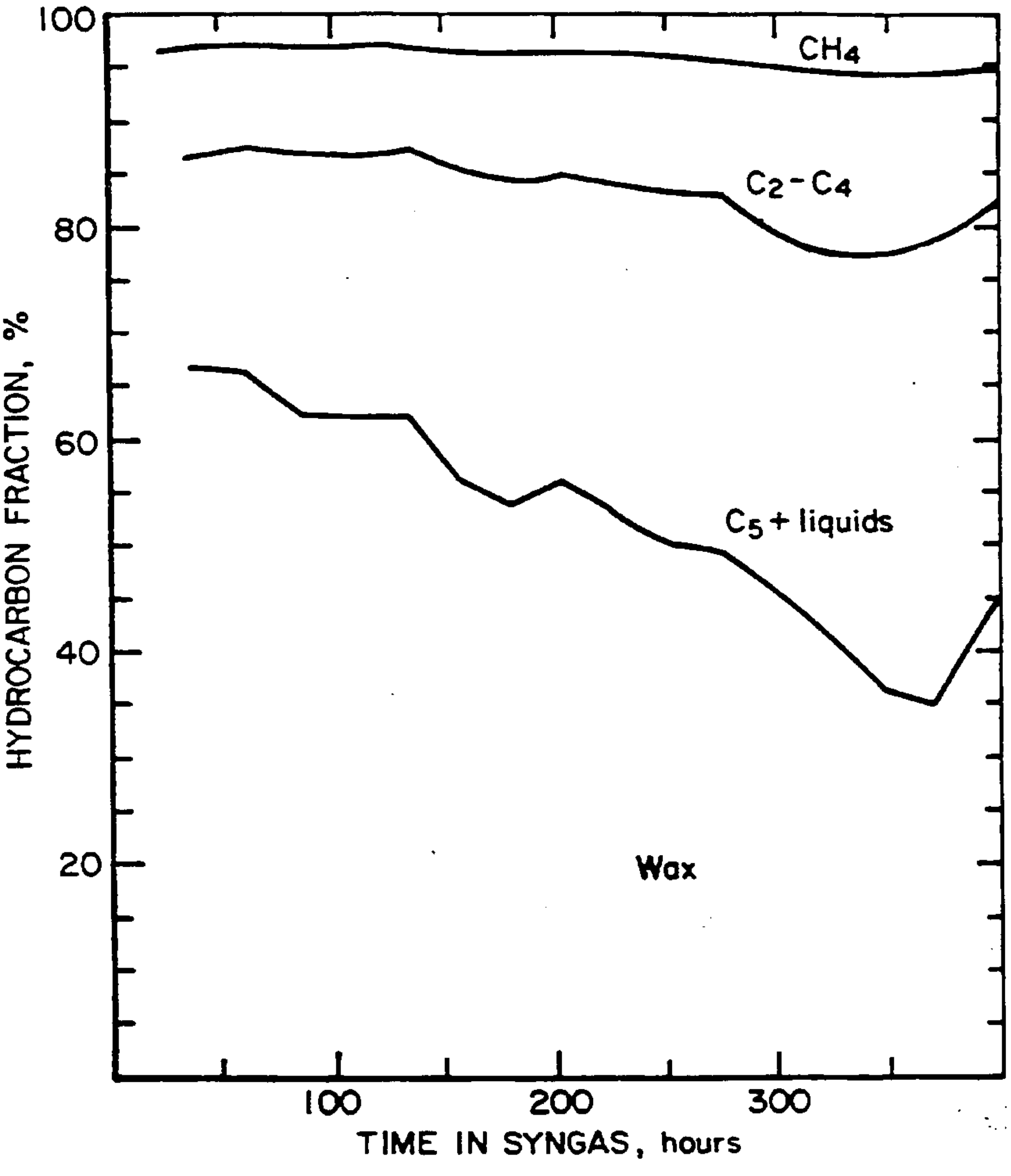

FIGURE 7. HYDROCARBON SELECTIVITY VS. TIME ON STREAM-INDUCED CATALYST

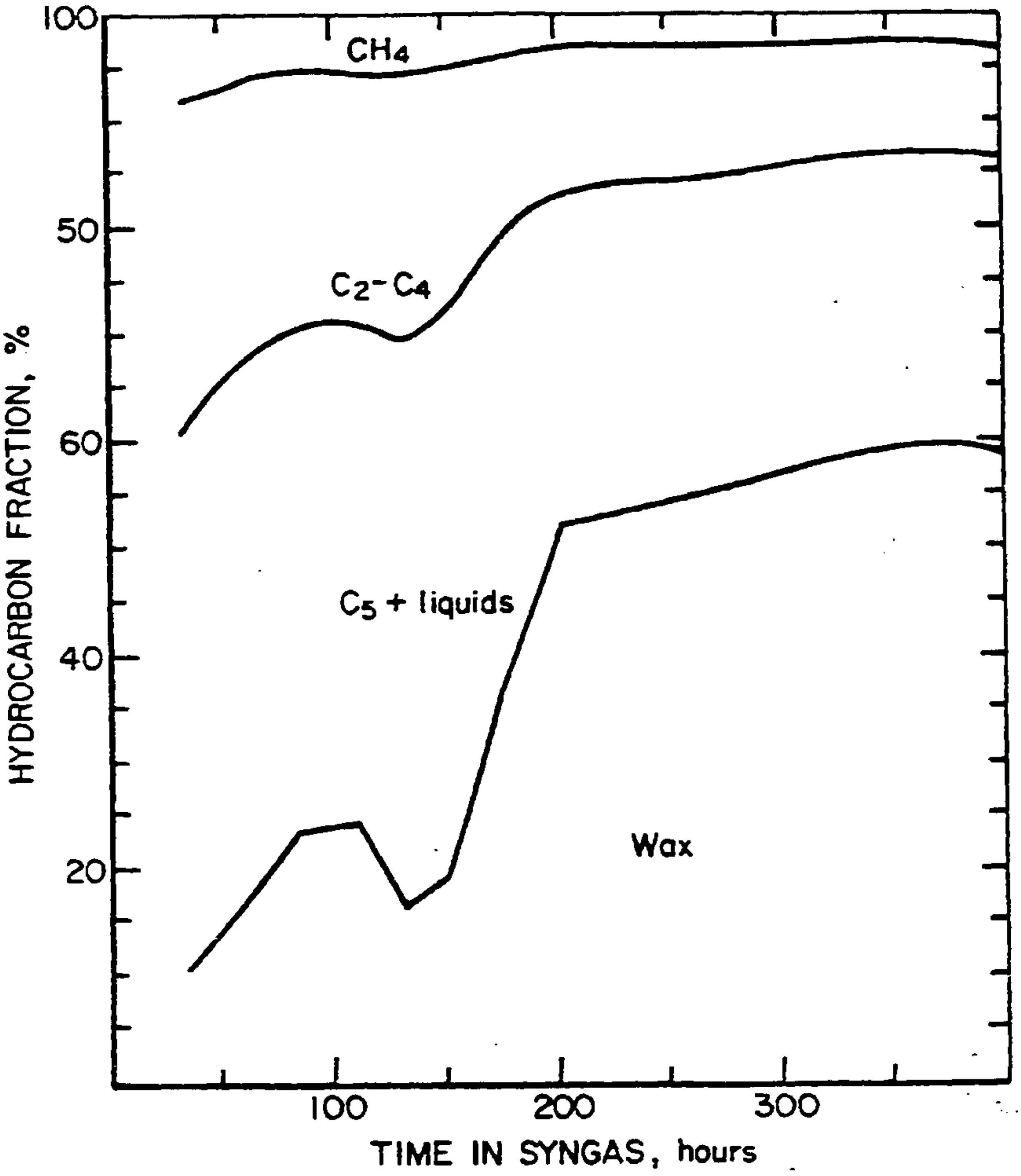

FIGURE 8. HYDROCARBON SELECTIVITY VS. TIME ON STREAM CO-PRETREATED CATALYST

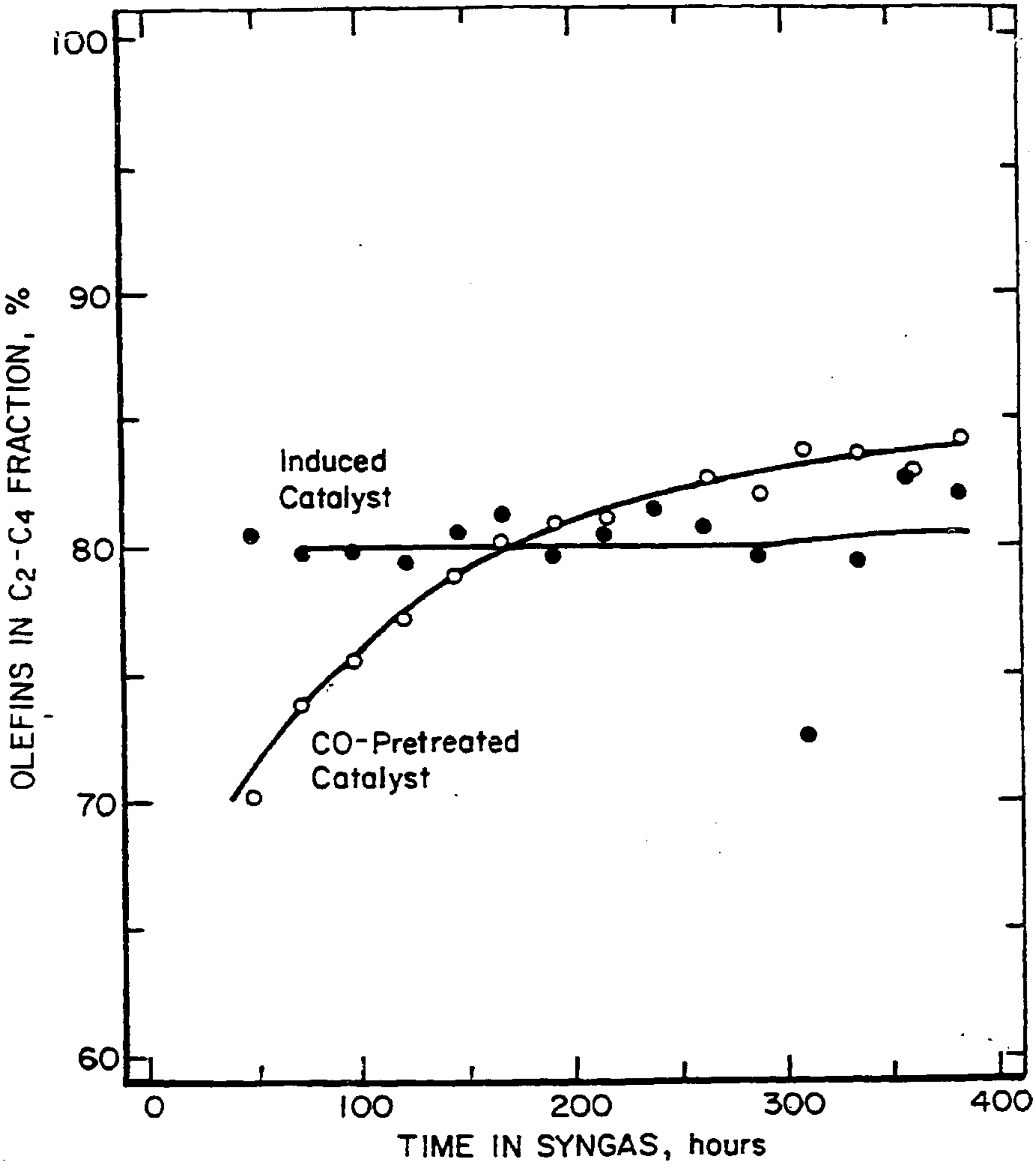

FIGURE 9. OLEFIN SELECTIVITY

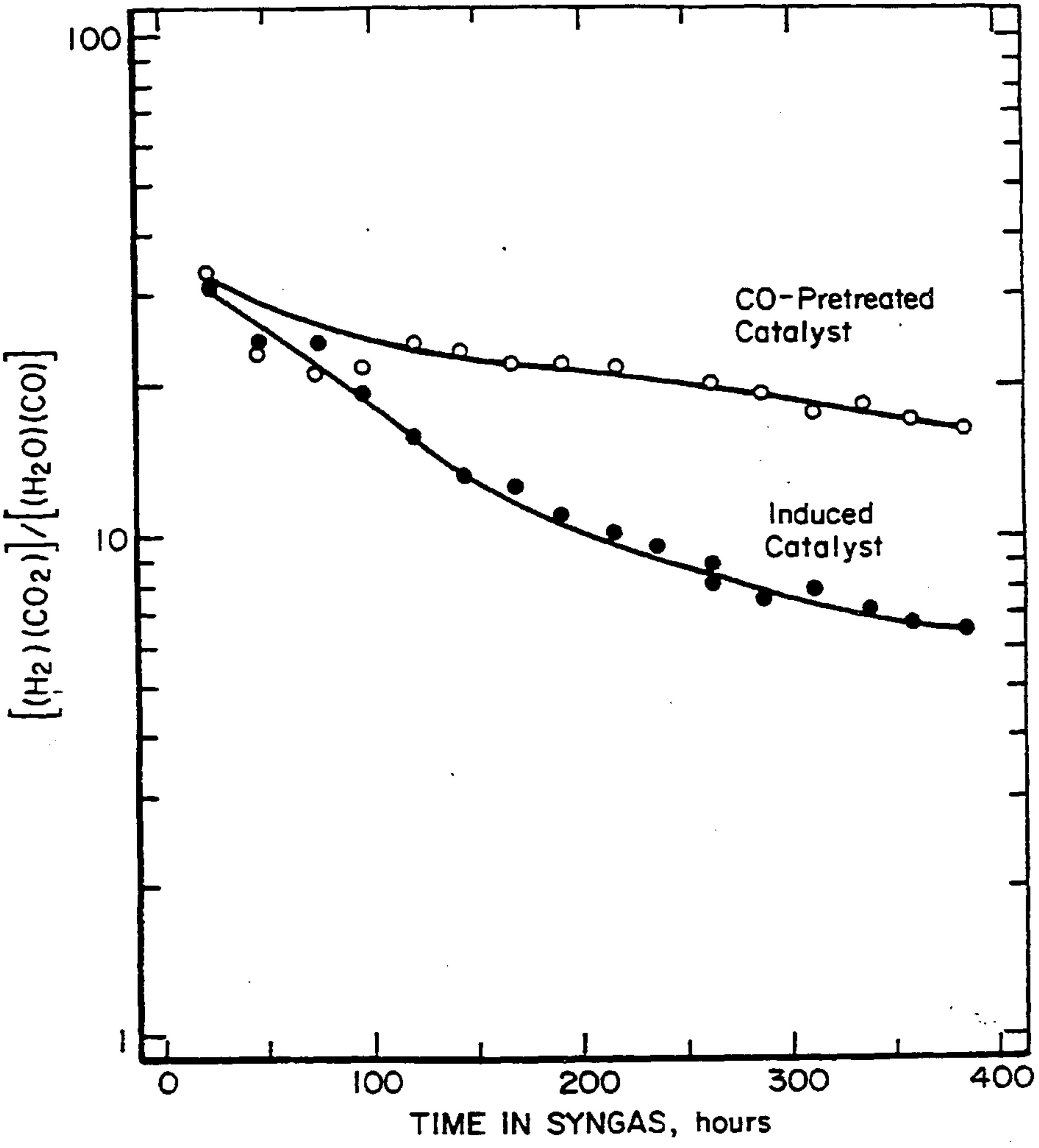

FIGURE 10. WATER-GAS SHIFT

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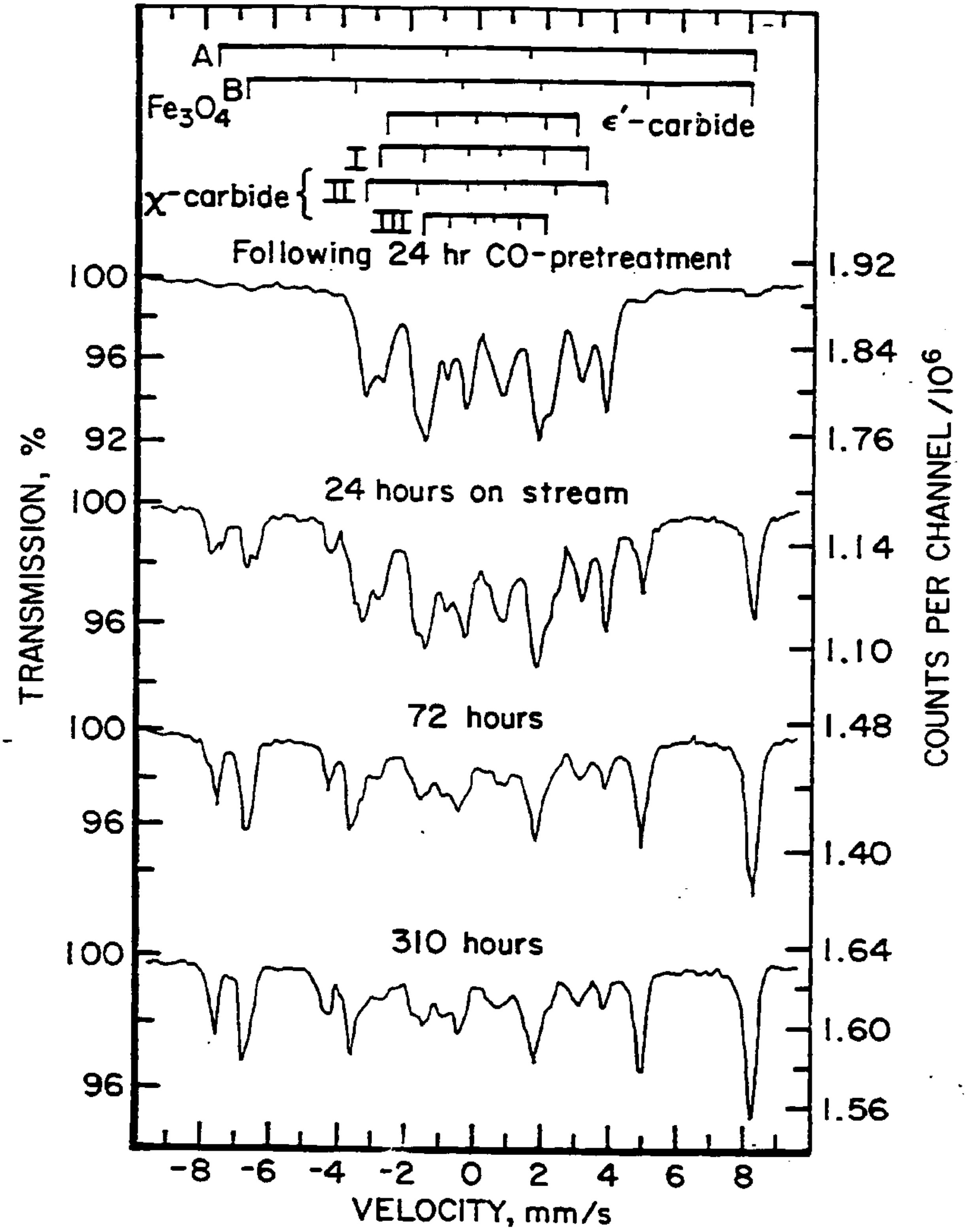

FIGURE 11. MÖSSBAUER SPECTRA-CO-PRETREATED CATALYSTS

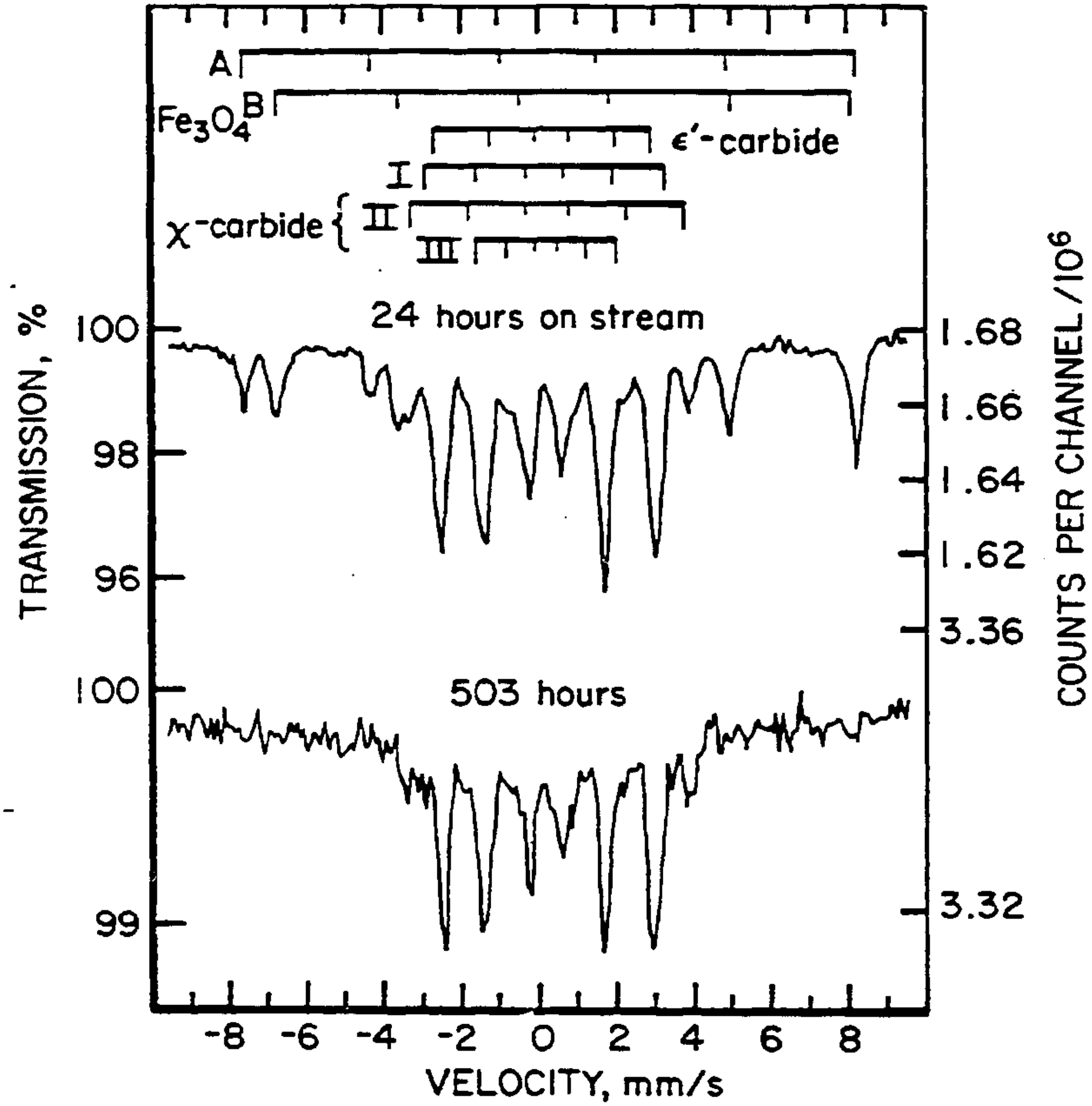

FIGURE 12. MÖSSBAUER SPECTRA- INDUCED CATALYST

FIGURE 13.
CONCLUSIONS

Activity: CO-pretreated catalyst — More active
— Maintains activity better

Selectivity: No major differences
CO-pretreated catalyst — Products initially light
(High % conversion → high H_2/CO)
— Product heavier with time on stream

Induced catalyst — Product lighter with time on stream

Composition:
CO-pretreated catalyst — Maintained activity despite oxidation
Inducted catalyst — No oxidation (lower % conversions)